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COHERENT ANTI-STOKES RAMAN SPECTROSCOPY OF SHOCK-COMPRESSED LIQUID OXYGEN[*]

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Vibrational spectra of liquid oxygen, shock compressed to several high-pressure/high-temperature states, were obtained using single-pulse multiplex coherent anti-Stokes Raman scattering (CARS). The experimental spectra were compared to synthetic spectra calculated using a semiclassical model for the CARS intensities and best fit vibrational frequencies, peak Raman susceptibilities, and Raman linewidths. Up to the maximum shock pressure of 9.6 GPa, the vibrational frequencies were found to increase monotonically with pressure. An empirical fit, which could be used as a pressure/temperature/frequency calibration standard, showed that the Raman frequency shifts could be accurately described by linear pressure and temperature dependences. Above ≈9 GPa, the liquid oxygen opacity at 632.8 nm increased rapidly, presumably because of proximity (collision)-induced absorption. Calculations showed that the induced absorption did not resonantly enhance the CARS spectra, but did attenuate the laser beams and the CARS signals.

1. INTRODUCTION

The behavior of simple molecular fluids at high pressure and temperature is of considerable interest because of the importance of these fluids in the planetary sciences, in chemical explosives technology, and for obtaining fundamental understanding of inter- and intra-molecular forces and energy transfer mechanisms. Historically, equation-of-state and energy transfer phenomenology have been determined from hydrodynamic and thermodynamic measurements such as shock-Hugoniot data. Recently, we demonstrated that it is possible, using coherent anti-Stokes Raman Spectroscopy (CARS), to obtain microscopic information about molecular nitrogen in the high-temperature dense fluid state.[1,2] Those results support well the microscopic notions assumed in present nitrogen equation-of-state models[3-5] including recent calculations of molecular vibrational frequencies.[6] In this paper we report similar measurements for molecular oxygen.

Equation-of-state and thermodynamic data have been obtained for oxygen at pressures up to 86 GPa and temperatures beyond 10,000 K using both static[7-11] and dynamic[12-14] compression techniques. These measurements have been complimented by calculations that describe the thermodynamic state of the fluid[14,15] and solid[16] phases. Electronic absorption and vibrational stretching frequencies have been measured for solid[7,17-19] and liquid[20] oxygen. The pressure dependence of the intramolecular mode frequencies for the solid phase has been calculated using a perturbation analysis.[21,22] There are no known calculations of the O_2 vibrational frequencies for the high-temperature dense fluid state. The high-pressure/high-temperature states of liquid O_2 investigated in this study (given in Table I) were achieved by dynamic compression techniques and the vibrational spectra were recorded using CARS. The experimental apparatus and data accuracy have been described previously.[23]

2. RESULTS AND DISCUSSION

Figure 1 shows experimental CARS results obtained at three different shock conditions. These spectra have been Fourier filtered[23] using a low-pass filter to reduce higher Fourier frequency components. The spectral lines on the left result from the 0-1 transition of the shock-compressed oxygen and the features to the right are the 0-1 transition from a thin layer of unshocked material. Also given in Fig. 1 are synthetic spectra obtained using a semiclassical theory to determine the CARS intensity.[1,2,23]

For liquid oxygen, the presence of proximity (collision) induced absorption bands[24-30] in the spectral region where these CARS experiments were performed leads to the possibility of electronic resonantly-enhanced CARS,[31] as well as absorption of the pump,

Stokes, and anti-Stokes beams. These possibilities were investigated by incorporating them into the CARS calculations of synthetic spectra and an empirical model for the absorption.[23] Unsuccessful attempts to favorably compare calculated results with experimental spectra suggested that the proximity induced absorption bands did not contribute to an electronic resonant enhancement of the CARS spectra.[23] A possible explanation for this behavior is that resonance enhancement occurs when the dipole moment responsible for absorption resides in the scattering molecule. Because for the oxygen, the induced absorption is a consequence of a single photon being split to effect two electronic transitions in two different molecules,[23,24] it is not clear where the absorption dipole moment resides. In addition, triple resonance is probably not possible because the absorption of one photon by the scattering molecule and its partner would require the presence of a second collision partner at precisely the right time and position to make possible the absorp-

tion of the second photon. We do, however, account for the effects of absorption on ω_p, ω_s, and ω_{as} when calculating the CARS intensity.

The transition frequencies, ratios of peak susceptibility to non-resonant background and linewidths used to calculate these spectra and the spectra for the remaining experiments are given in Table I. Because the temperatures obtained in these experiments were too low to produce hot-band transitions of sufficient intensity to be readily visible, estimates of vibrational temperatures were not possible.[3] In the calculations, however, we included one hot-band transition at the gas-phase separation value of 24.1 cm^{-1},[32] and at a peak susceptibility reflecting Boltzmann equilibrium population of the vibrational energy levels.[2] So they may in no way accidentally be interpreted as experimental data, these values are not listed in Table I. Inclusion of these transitions confirmed that the shock-compressed oxygen did not have an abnormally high-vibrational temperature.

Table I. Summary of shock conditions and spectroscopic parameters. [P is pressure in GPa, ρ is 10^{-3} times the density in kg/m^3, T_{eos} is equation-of-state temperature in K, v is shock velocity (km/s), ω_p, and ω_j are the pump and transition frequencies (cm^{-1}), respectively, χ_j^{pk}/χ^{nr} is the ratio of the peak susceptibility to nonresonant background, and Γ_j is the linewidth (HWHM, cm^{-1}).]

| Initial Conditions		Single-Shock Experiment			Double-Shock Experiment			
		ω_j	$\frac{\chi_j^{pk}}{\chi^{nr}}$	Γ_j		ω_j	$\frac{\chi_j^{pk}}{\chi^{nr}}$	Γ_j
$P = 0.00010$ $\rho = 1.169$ $T = 84.4$ $\omega_p = 17176.9$	Not Shocked	1551.3	150.0	0.115				
$P = 0.00010$ $\rho = 1.169$ $T = 84.4$ $\omega_p = 17176.9$	$P = 4.8$ $\rho = 1.88$ $T_{eos} = 366$ $v = 3.30$	1564.3	35.0	0.6	$P = 9.8$ $\rho = 2.21$ $T_{eos} = 492$	1579.3	4.0	3.2
$P = 0.00010$ $\rho = 1.157$ $T = 87.0$ $\omega_p = 17176.9$	$P = 7.8$ $\rho = 2.01$ $T_{eos} = 782$ $v = 3.98$	1569.6	12.6	1.5				
$P = 0.00010$ $\rho = 1.172$ $T = 83.9$ $\omega_p = 17176.9$	$P = 8.3$ $\rho = 2.04$ $T_{eos} = 811$ $v = 4.08$	1572.0	9.4	2.2				
$P = 0.00010$ $\rho = 1.169$ $T = 84.4$ $\omega_p = 15953.5$	$P = 9.1$ $\rho = 2.07$ $T_{eos} = 926$ $v = 4.22$	1572.8	7.0	2.5				
$P = 0.00010$ $\rho = 1.165$ $T = 85.2$ $\omega_p = 17176.9$	$P = 9.6$ $\rho = 2.09$ $T_{eos} = 1013$ $v = 4.32$	1574.2	5.7	2.7				
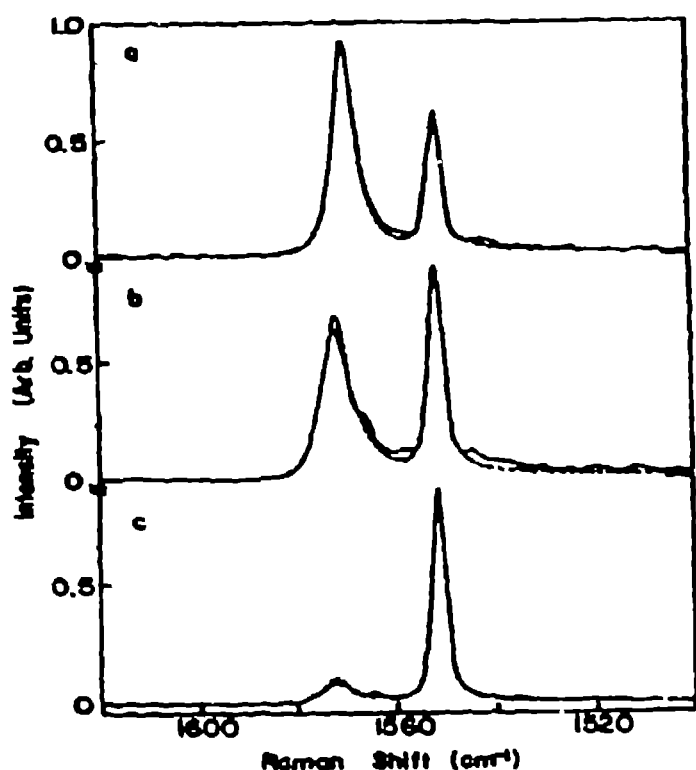
Fig. 1. Representative CARS spectra: a) — 7.8 GPa and 782 K, — synthetic spectrum. b) — 8.3 GPa and 811 K, — synthetic spectrum. c) — 9.1 GPa and 926 K, — synthetic spectrum.

Figure 2 shows the measured Raman shifts vs pressure for the shock states given in Table I. There is a monotonic increase of the vibrational frequency with increasing pressure. This is in contrast to the behavior observed in nitrogen,[3] where the frequency first increases with pressure, then reverses and begins to decrease with further increases in pressure. However, the maximum pressure of these experiments is considerably less than the pressure, $\approx$ 17.5 GPa, where the frequency reversal occurred for nitrogen. When the fluid is singly or doubly shocked to the same pressure, the difference in the measured Raman shift results from the effects of temperature on the potential and on the portion of the potential sampled on average.[3]

The measured Raman frequency shifts for ambient, singly-shocked and doubly-shocked oxygen were least squares fit[33] to the following empirical relation

$$\omega_{jcalc} = \omega_e - 2\omega_e x_e$$

$$+3.234(\pm0.063)P - 0.00913(\pm0.00066)\,T \quad (1)$$

where the pressure, P and temperature, T are given in GPa and K, respectively. ω_e equal to 1576.3 cm^{-1} was
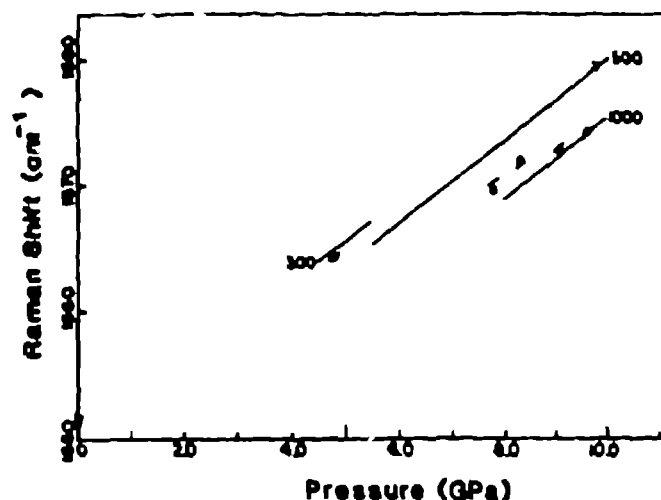

Fig. 2. Raman shift versus pressure. • - single shock; o - double shock; — isotherms at temperature in K.

chosen to match experimental data at ambient pressure and $\omega_e x_e$ equal to 12.073 cm^{-1} was taken from Herzberg.[32] The range of values shown for the pressure and temperature coefficients are the standard errors for these coefficients resulting from the least squares fit. The standard error of the fit is 0.33 cm^{-1}. The short segment near each data point in Fig. 2 gives the calculated frequency value from Eq. (1) at the measured pressure and temperature and the long curves show the positions of the 300-K, 800-K, and 1000-K isotherms also obtained using Eq. (1). Each isotherm is drawn over the approximate range of validity of the empirical fit.

3. CONCLUSIONS

At single-shock pressures up to 9.6 GPa and 1013 K, oxygen exists as a molecular fluid whose vibrational frequency increases with pressure. CARS spectra obtained using laser frequencies that were attenuated by proximity-induced absorption bands could be modeled as ordinary CARS spectra, i.e., no electronic resonant enhancement was apparent. An empirical fit showed that the Raman frequency shifts could be accurately described with linear pressure and temperature dependences. This fit could presumably be used as a pressure/temperature/frequency calibration standard in more ill-defined experiments, e.g., laser heating in a diamond-anvil cell.

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